

Time-dependent density-functional theory with self-interaction correction

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We discuss an extension of time-dependent density-functional theory by a self-interaction correction (SIC). A strictly variational formulation is given taking care of the necessary constraints. A manageable and transparent propagation scheme using two sets of wavefunctions is proposed and applied to laser excitation with subsequent ionization of a dimer molecule.

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Density Functional Theory (DFT)^{1,2,3,4} has evolved over the last decades to a standard theoretical tool for the description of electronic properties in many physical and chemical systems, especially in systems with sizable numbers of electrons. The extension of DFT to Time-Dependent situations (TDDFT)^{5,6,7} is a more recent achievement still motivating many investigations, both for formal and practical aspects⁸. It turns out that TDDFT is one of the few, well founded theories, allowing to describe dynamical scenarios in complex systems, which is a key issue for understanding microscopic mechanisms, beyond mere energetic considerations. This is especially true if electron emission comes into play as, e.g., in case of irradiation processes.

A practical treatment of DFT, and even more so TDDFT, requires simple approximations to the exchange and correlation functional. The simplest one is the Local Density Approximation (LDA) which proved very useful in calculations of structure and low-amplitude excitations (optical response, direct one-photon processes)⁴. It is also often used as a first order approach for more violent dynamical processes where huge energy deposits lead to a large number of emitted electrons as, e.g., in clusters subject to intense laser fields or collided by highly charged particles⁹. However, LDA is plagued by a self-interaction error because its Kohn-Sham field involves the total density including the particle on which the field just acts. As a consequence, the LDA produces the wrong Coulomb asymptotic of the mean field and thus underestimates the ionization potential (IP) of a system. This spoils, e.g., the dynamical description of excitations involving ionization processes, in particular close to the threshold. A correct treatment requires a self-interaction correc-

tion (SIC). Such a SIC complementing LDA for static calculations was proposed in¹¹ and has been used since then at various levels of refinement for structure calculations in atomic, molecular, cluster and solid state physics, see e.g.^{12,13,14,15}.

The original SIC scheme leads to an orbital dependent mean field which causes several formal and technical difficulties. There are attempts to circumvent these problems by treating SIC with optimized effective potentials (OEP), see^{16,17}. That, however, overrules some crucial physical features of SIC, particularly the trend to produce localized single-particle states¹⁶.

Application of SIC in time-dependent situations are mostly done in approximate manner, linearized¹⁸, using averaged-density SIC¹⁹, or relying on various versions of time dependent OEP-KLI^{20,21,22}. The TDOEP-KLI, however, also suffers from inconsistencies as it leads, e.g. to violation of zero force theorem and energy conservation²³. The aim of this letter is to present a thorough variational formulation of fully fledged TDSIC without further approximation, together with a manageable propagation scheme which allows to obey all boundary conditions, namely the zero-force theorem, conservation of energy and orthonormality of the occupied single-particle orbitals. This will in particular serve as a benchmark for the development and validation of further approximate treatments for example in the spirit of (TD)OEP approaches. A first application to a one-dimensional molecule proves the feasibility and stability of the scheme. A comparison with exact exchange confirms the need and satisfying performance of full TDSIC in ionization dynamics.

We work in the Kohn-Sham scheme of DFT, built on a set of single particles wavefunctions $\{\psi_\alpha, \alpha = 1, \dots, N\}$. In the SIC case, the starting energy functional reads

$$E_{\text{SIC}} = E_{\text{kin}} + E_{\text{ion}} + E_{\text{LDA}}[\rho] - \sum_{\beta=1}^N E_{\text{LDA}}[\rho_\beta] \quad (1)$$

where the electronic kinetic energy E_{kin} is complemented by the external ionic contribution E_{ion} and the LDA approximation $E_{\text{LDA}}[\rho]$ to the exact electron-electron interaction energy. The densities are further defined as $\rho_\alpha = |\psi_\alpha|^2$ and $\rho = \sum_\alpha \rho_\alpha$. Note that all summations run over occupied states only.

The TDSIC equations are obtained from the principle of stationary action using the SIC energy functional (1)

$$0 = \delta \int_{t_0}^t dt' \left(\sum_\alpha (\psi_\alpha | i\hbar \partial_t | \psi_\alpha) - E_{\text{SIC}} + \sum_{\beta, \gamma} (\psi_\beta | \psi_\gamma) \lambda_{\gamma\beta} \right) \quad (2)$$

within explicitly including the orthonormality constraint with Lagrange multipliers $\lambda_{\gamma\beta}$. Variation of E_{SIC} with respect to ψ_α^* leads to single particle equations for the ψ_α 's in which the one-body Hamiltonian is obtained as

$$\frac{\delta E_{\text{SIC}}}{\delta \psi_\alpha^*} = \hat{h}_\alpha \psi_\alpha, \quad \hat{h}_\alpha = \hat{h}_{\text{LDA}} - U_\alpha, \quad (3a)$$

$$\hat{h}_{\text{LDA}} = -\frac{\hbar^2 \Delta}{2m} + U_{\text{LDA}}[\rho] \quad (3b)$$

$$U_\alpha = U_{\text{LDA}}[|\psi_\alpha|^2] \quad (3c)$$

$$U_{\text{LDA}}[\varrho] = \left. \frac{\delta E_{\text{LDA}}}{\delta \rho} \right|_{\rho=\varrho} \quad (3d)$$

The emerging one-body Hamiltonian \hat{h}_α depends on the state ψ_α on which it acts through the SIC term U_α . The \hat{h}_α 's can be simply recast in a SIC Hamiltonian \hat{h}_{SIC} by employing projectors as

$$\hat{h}_{\text{SIC}} = \hat{h}_{\text{LDA}} - \sum_\alpha U_\alpha |\psi_\alpha\rangle \langle \psi_\alpha| \quad (3e)$$

That form embodies the state-dependence in the projector and displays clearly the non-hermitian nature of \hat{h}_{SIC} , which is also not invariant under a unitary transform amongst the $|\psi_\alpha\rangle$.

Variation of the action with respect to ψ_α^* thus yields the TDSIC equations as

$$(\hat{h}_{\text{SIC}} - i\hbar \partial_t) |\psi_\alpha\rangle = \sum_\beta |\psi_\beta\rangle \lambda_{\beta\alpha} \quad (4a)$$

$$\lambda_{\beta\alpha} = (\psi_\beta | \hat{h}_\alpha - i\hbar \partial_t | \psi_\alpha) \quad (4b)$$

together with the symmetry condition

$$0 = (\psi_\beta | U_\beta - U_\alpha | \psi_\alpha) \quad (4c)$$

which has to be fulfilled at each instant. It should be noted that once one has achieved the symmetry condition (4c), the SIC Hamiltonian (3e) acquires an interesting property. Although it remains non-hermitian as a whole, it becomes hermitian within the space of occupied states

$$(\psi_\beta | \hat{h}_{\text{SIC}} | \psi_\alpha) = (\psi_\alpha | \hat{h}_{\text{SIC}} | \psi_\beta)^* \quad (5)$$

The above TDSIC equations are quite involved as the time propagation, Eqs. (4a-4b), is constrained by the symmetry condition (4c), unlike propagation with a strictly hermitian Hamiltonian (LDA or Hartree-Fock) for which the symmetry condition is automatically fulfilled. A simple minded step

$$|\psi_\alpha(t)\rangle = \exp \left\{ -\frac{i}{\hbar} \int_{t_0}^t dt' \hat{h}_{\text{SIC}}(t') \right\} |\psi_\alpha(t_0)\rangle,$$

is thus not directly applicable because it does not ensure the preservation of the symmetry condition. One has to employ an interlaced step which allows to fulfill simultaneously Eqs. (4).

In order to overcome this difficulty, we note that there is always the freedom of unitary transformations amongst the set of occupied orbitals $\{\psi_\alpha, \alpha = 1, \dots, N\}$ without changing the state of a system. The ψ_α are the unique ingredients of the SIC mean field. But propagation of the whole state may be formulated in terms of another set $\{\varphi_i\}$ chosen to have convenient propagation properties and connected to the ψ_α by a unitary transformation within occupied states :

$$|\varphi_i(t)\rangle = \sum_{\beta=1}^N |\psi_\beta(t)\rangle v_{i\beta}^*(t) \quad (6a)$$

We call the $\{\varphi_i\}$ the “propagating” set and the $\{\psi_\alpha\}$ the “symmetrizing” set, the idea being to perform a joined propagation of $\{\varphi_i\}$ and $\{\psi_\alpha\}$ such that each of the two (connected) sets of orbitals contributes either the propagation or the

symmetry condition. It is nevertheless crucial to note that the ψ_α remain the key constituents composing the SIC potentials (3c) and entering the symmetry condition (4c) through the U_α . The propagation set φ_i gives the freedom to choose the propagation within occupied states at convenience. We choose it such that

$$(\hat{h}_{\text{SIC}} - i\hbar\partial_t)|\varphi_i\rangle = 0, \quad (6b)$$

which allows to fulfill Eqs. (4a-4b) and which is possible as soon as the ψ_α fulfill the symmetry condition (4c). This allows then to propagate the $\{\varphi_i\}$ as :

$$|\varphi_i(t)\rangle = \exp\left\{-\frac{i}{\hbar}\int_{t_0}^t dt' \hat{h}_{\text{SIC}}(t')\right\}|\varphi_i(t_0)\rangle \quad (6c)$$

and to care for the symmetry condition at the side of the ψ_α , the latter fixing the coefficients of the unitary transformation. This reads formally

$$v_{i\beta}(t) : 0 = (\psi_\beta|U_\beta[|\psi_\beta|^2] - U_\alpha[|\psi_\alpha|^2]|\psi_\alpha). \quad (6d)$$

It is to be noted that the propagator in Eq. (6c) is not strictly unitary because \hat{h}_{SIC} is not hermitian. But the hermiticity within occupied space, Eq. (5), guarantees that the propagation (6c) preserves orthonormality within occupied space, *i.e.* $(\varphi_i(t)|\varphi_j(t)) = \delta_{ij}$.

The above described propagation scheme for TDSIC exhibits some interesting properties. As already noted, it preserves orthonormality, which is a crucial requirement for any time evolution scheme. One can also show that energy and the zero-force theorem are conserved (as long as there are no time-dependent external fields). Finally, we remark that the choice (6c) for the propagating set is not the only possibility. There is some freedom for other choices as, *e.g.*, optimizing single-particle energies²⁴.

As a final point, we apply TDSIC to a typical example of laser excitation and subsequent ionization of a molecule. We use a simple one-dimensional model for a molecule in the spirit of²⁵. The model case is a dimer with two electrons having the same spin. As an interaction, we use the following smoothed Coulomb potential, $w_{ij} = e^2/\sqrt{(x_i - x_j)^2 + a_{ij}^2}$, where the parameters a_{ij} for electron-electron, electron-ion and ion-ion interactions are tuned to reproduce typical molecular energies. Taking that interaction, we develop

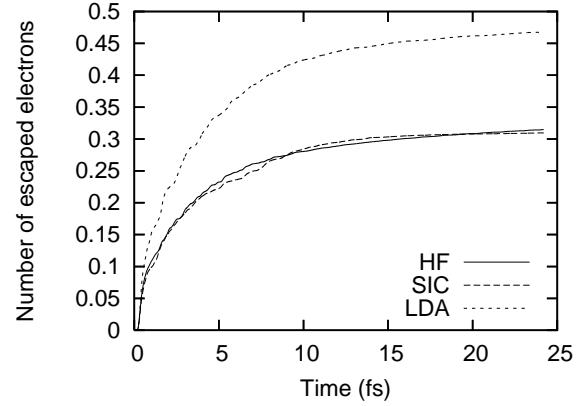


FIG. 1: Time evolution of the number of emitted electrons for a dimer molecule with two electrons. Compared are results from full TDHF, TDLDA and TD-SIC.

with LDA an energy functional for the exchange term. Working at the level of exchange only allows to have fully fledged time-dependent HF (TDHF) calculations as benchmark to which DFT calculations can be compared.

A very short laser pulse is simulated as an instantaneous boost²⁶. This has the advantage that energy conservation can be used as test for the calculations. We have checked conservation of energy, orthonormality and symmetry condition which are all found fully satisfied. As a further observable, we consider the degree of ionization which, as stated above, is a sensitive quantity to probe the effect of SIC. The results are shown in Fig. 1 comparing the TDHF benchmark with TDLDA and TDSIC. It is obvious that TDSIC comes very close to the benchmark.

Finally we want to remark that the double-set strategy can also be applied to the static SIC problem. The static SIC equations are obtained by minimizing E_{SIC} with a constraint on orthonormality of the single-particle wavefunctions ψ_α , $\delta_{\psi_\alpha^*} \left(E_{\text{SIC}} - \sum_{\beta,\gamma} (\psi_\beta|\psi_\gamma) \lambda_{\gamma\beta} \right) = 0$, following standard variational derivations^{12,13}. One then simply obtains $\hat{h}_{\text{SIC}}|\psi_\alpha\rangle = \sum_{\beta} (\psi_\beta|\psi_\alpha) \lambda_{\alpha\beta}$, again together with the symmetry condition Eq.(4c). Note that the matrix of Lagrange multipliers $\lambda_{\beta\alpha} = (\psi_\beta|\hat{h}_{\text{SIC}}|\psi_\alpha)$ is usually non-diagonal. The states ψ_α which emerge as solutions of stationary equations are optimized to produce the correct SIC potentials. They do not give any clue on single-

particle energies. One can now introduce a second set of $\{\varphi_i\}$ connected by the stationary analogue of the unitary transformation (6a) and require, e.g., that these φ_i diagonalize \hat{h}_{SIC} (expressed in terms of the ψ_α , Eq.(3e)), or equivalently the matrix of Lagrange multipliers $\lambda_{\alpha\beta}$. The eigenvalues thus obtained can be interpreted as single-particle energies and they are found to agree fairly well with HF values in the case of exchange only calculations that we consider here. Note finally that these static SIC equations also emerge naturally as the stationary limit of TDSIC.

We have proposed in this letter a consistent variational formulation of time-dependent SIC (TD-SIC) together with a manageable and transparent scheme for the solution of the TDSIC equations. This scheme provides conservation of energy, zero-force theorem, and orthonormality of the occupied states. The stationary limit of static SIC is also properly recovered both by the theory itself and by the propagation scheme. We applied the scheme to laser-induced ionization of a one-dimensional dimer molecule as a test case. The calculations have proven to run stable and to fulfill all theoretical constraints. As a critical observable, we have

investigated the time evolution of ionization and found nice agreement of the exchange only TDSIC results with an exact TDHF calculation.

Although even full 3D calculations have proven to be feasible, it is to be admitted that fully fledged TDSIC is rather involved and thus computationally complex. We consider it as starting point for further development towards simplified schemes. A promising option is provided by a time-dependent form of optimized effective potentials^{16,20}. Work in that direction is in progress. Nevertheless the full TDSIC serves as a crucial benchmark for such developments.

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